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Highly Diastereoselective Hydrosilane-Assisted Rhodium-Catalyzed Spiro-Type Cycloisomerization of Succinimide and Pyrazolone-Based Functional 1,6-Dienes

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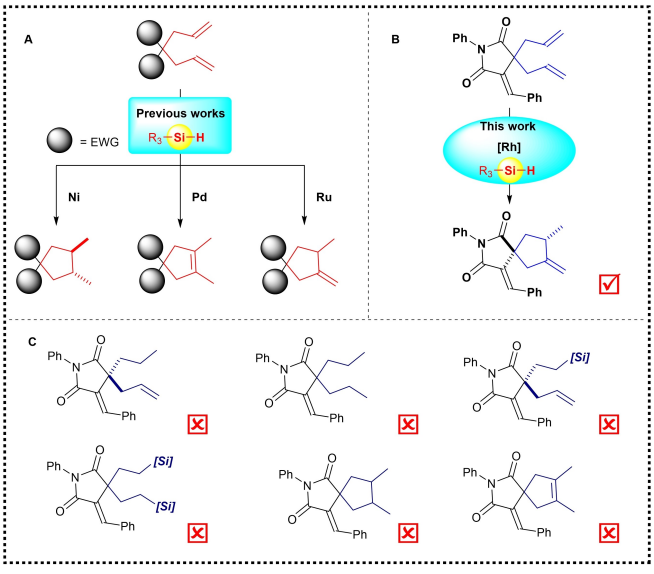
Dedicated to Prof. Andy Hor for his 65th birthday

Abstract: Organosilicon compounds are important reagents and synthetic intermediates that play a key role in the construction of new materials and complex products. Here we show a highly diastereoselective rhodium-catalyzed cycloisomerization of 1,6-dienes, in which the use of $(EtO)_3SiH$ accelerates the intramolecular cyclization reaction to afford a novel spiro-fused succinimide and pyrazolone derivatives in moderate to excellent yields as a single diastereoisomer. The proposed mechanism involves an active Rh–H species from the hydrosilane that is the H-donor in this spiro-type cycloisomerization reaction.

Transition-metal-catalyzed cycloisomerization of α,ω-dienes have been one of the most important and atom-economic reaction processes in the construction of functionalized cyclic products that are fundamental constituents of pharmaceutical compounds and nature products, also in the field of functional materials.[1] In this regard, extensive studies have been carried out on the cycloisomerization-type cyclization of α,ω-dienes, promoted by various transition-metal catalysts, including nickel,[2] palladium,[3] ruthenium,[4] titanium,[5] Lewis super acids,[6] and other metal catalysts.[7] Among these catalytic methods, the synthetic potential of rhodium in cycloisomerization of α,ω-dienes has become an attractive strategy in the synthesis of carbocycles or heterocycles.[8] Although Malone and co-workers reported the first example of the $RhCl_3$-catalyzed cycloisomerization of structurally simple α,ω-diallyl ether dienes in 1971,[9] there are a few reports on the Rh-catalyzed cycloisomerization of 1,6-dienes, and compatibility of functional group is generally problematic for this reaction.[10] On the other hand, the transition-metal-catalyzed cyclization of α,ω-dienes generally underwent cycloisomerization with low chemoselectivity to deliver a mixture of isomers, which demonstrates the difficulty in controlling chemo- and regioselectivity because of structurally diverse isomers.[11] Notably, although recent efforts have been performed on the development of new synthetic methods for constructing complex carbocycles, the scope of the chemistry of the Rh-catalyzed cycloisomerization reactions had not expanded to diastereoselective reductive cyclization assisted by hydrosilane, while some reports described 1,6-dienes could be transformed into different carbocycles in the presence of other transition-metal catalysts[2–4] (Scheme 1A). Therefore, it is worth to explore and develop a Rh-catalyzed reaction of 1,6-dienes with high level of chemoselectivity among all the possibilities of reaction pathways.



Scheme 1. Competitive reaction pathways in the hydrosilane -assisted transition-metal-catalyzed cycloisomerization of 1,6-dienes: from the transformations of simple 1,6-dienes to heterocycle-functionalized 1,6-dienes (this work).

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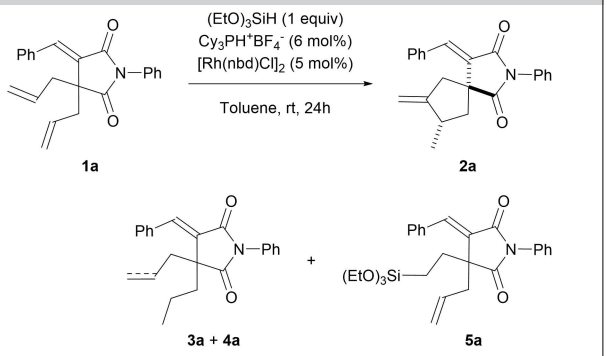
In addition, there is no report on the catalytic construction of spiro-fused succinimide-derived functional *N*-heterocycles with stereoselective version of Rh-catalyzed cycloisomerization or reductive cyclization of functionalized 1,6-dienes to date. In this context, succinimide and its derivatives are one of versatile building blocks for synthetic chemistry and functional materials,[12] allowing for subsequent transformations of skeletal variation and investigation as drug candidates. One of the challenges is the cyclization reaction could either compete with reduction or hydrosilylation on the C=C doubles of 1,6-dienes and the amide group due to the nature of Si–H bond activation of hydrosilane with the aid of rhodium catalyst.[13] On the basis of our previous studies on silicon-mediated organic synthesis,[14] herein we want to present a novel Rh- catalyzed cycloisomerization of succinimide or pyrazolone -derived 1,6-dienes in the presence of hydrosilane to finish a highly chemoselective synthesis of spiro-fused heterocycles with high yield and diastereoselectivity.

At the outset of the project, we explored the rhodium-catalyzed reaction using succinimide derived 1,6-diene **1a** with $(EtO)_3SiH$ (triethoxysilane) as model substrates, the experimental results are summarized in Table 1 (for the details of optimizations, see the ESI). The reaction was carried out smoothly in the presence of $[Rh(nbd)Cl]_2$ with $Cy_3PH^+BF_4^-$ (tricyclohexylphosphine tetrafluoroborate) as a ligand source in toluene at room temperature to afford a methylenecyclopentane derivate **2a** in 87% isolated yield as a single diastereoisomer (entry 1 of Table 1), whereas the corresponding product was obtained in lower yield when Cy_3P (tricyclohexylphosphine) was used as the ligand in this process (entry 2). Surprisingly, $t\text{-}Bu_3PH^+BF_4^-$ mainly led to reductive compounds (**3a** and **4a**), Xantphos also in favor of the reductive compounds (**3a** and **4a**) and a small amount of adduct **5a**. It turned out that PPh_3 and TPTP (tri(*p*-tolyl)phosphine) were not suitable ligand to construct **2a** (entry 3–6). Further investigation showed that, when the reaction was performed at a higher temperature (60 °C), it would increase the ratio of reductive product (**3a** and **4a**).

Table 1. Optimization of reaction conditions.[a]



Entry	Derivation from standard conditions	**2a**/(**3a**+**4a**)/**5a**[Yield%][b,c]
1	none	97/3/0[d]
2	Cy_3P instead of $Cy_3PH^+BF_4^-$	71/2/0
3	$t\text{-}Bu_3PH^+BF_4^-$ instead of $Cy_3PH^+BF_4^-$	0/68/4
4	Xantphos instead of $Cy_3PH^+BF_4^-$	0/86/14
5	PPh_3 instead of $Cy_3PH^+BF_4^-$	2/0/22
6	TPTP instead of $Cy_3PH^+BF_4^-$	0/0/69
7	at 60 °C instead of rt	93/7/0/0
8	DCM instead of toluene	89/9/0/0
9	$[Rh(cod)]Cl_2$ instead of $[Rh(nbd)Cl]_2$	88/12/0/0
10	$Pd_2(dba)_3$ instead of $[Rh(nbd)Cl]_2$	NR
11	Without $(EtO)_3SiH$	7/0/0
12	0.5 eqiuv of $(EtO)_3SiH$ was used	47/0/0
13	Et_3SiH instead of $(EtO)_3SiH$	92/2/0/0
14	$MePhSiH_2$ instead of $(EtO)_3SiH$	76/24/0/0
15	$PhSiH_3$ instead of $(EtO)_3SiH$	70/4/0/0

[a] Unless otherwise noted, the reaction conditions were as follows: **1a** (0.2 mmol), silane (0.2 mmol), and in toluene (2.0 mL). [b] Determined by GC-MS. [c] Unless otherwise noted, the dr of **2a** is generally >20:1, which was determined by ^1H NMR on the crude reaction mixture. [d] 78% isolated yield.

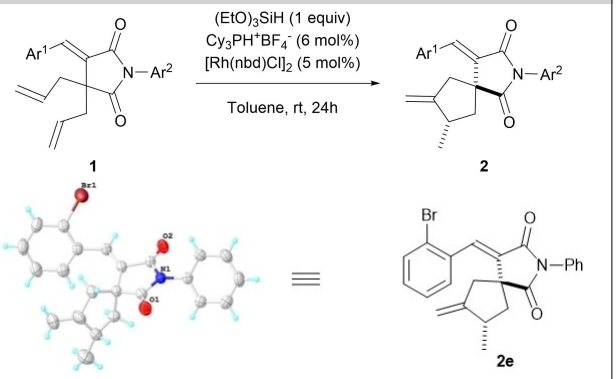
Moreover, the replacement of toluene by other solvents in the rhodium-catalyzed cycloisomerization of succinimide derived 1,6-diene **1a** normally gave a mixture of the spro-product **2a** with reductive compounds (**3a** and **4a**) (entry 8). In addition, $[Rh(cod)Cl]_2$ provided the corresponding product **2a** in a slight lower yield mixed with 12% reductive mixture (**3a** and **4a**) (entry 9), while other rhodium catalysts were tested and did not provide any improvement in this cycloisomerization process. Note that the cyclization did not occur in the presence of $Pd_2(dba)_3$ (entry 10).

Furthermore, the hydrosilane was found to be crucial in this rhodium-catalyzed cycloisomerization process, as the absent of $(EtO)_3SiH$ only gave trace amount of **2a**, while submitting 0.5 equivalent $(EtO)_3SiH$ to the reaction, 47% yield of **2a** was observed. Finally, other silanes were examined, such as Et_3SiH (triethyl silane), $MePhSiH_2$ (methylphenyl silane) and $PhSiH_3$ (phenyl silane), in which only Et_3SiH provide **2a** with a very good chemical control and excellent diastereoselectivity similar to $(EtO)_3SiH$, but a slight decrease on the conversion of **1a**. $MePhSiH_2$ gave a poor chemical selectivity (76:24). A lower conversion of **1a** was observed in the case of $PhSiH_3$. On the basis of these experimental results, we suggested that the activation of rhodium catalyst by various hydrosilanes is obviously different because of its differentiated ability in the interaction of a hydrosilane with rhodium complex.[15] And the steric hindrance of aryl or alkyl substituents on hydrosilane would affect the formation of Rh–H species (Si-M–H species), which also made influence on the subsequent addition of metal hydride to alkenes.

With those optimized conditions in hand, we examined the scope of the reaction (Table 2). First, the reaction was carried out with β-styryl derivative bearing a halogen substituent at the *meta*-position. Pleasingly, *meta*-bromo and *meta*-chrolo derivatives (**1b**, **1c**) were converted into the spiro-products **2b** and **2c** in moderate yields with excellent diastereoselectivity. A similar reactivity was observed for the *meta*-methoxy aryl derivatives (**1d**). Bromo and methoxy substituents at *ortho*-position were also tolerated, giving the corresponding products in good yields (**2e**, **2f**).

Then we examined the effect of *para*-substitution on the cyclization transformation. *Para*-chloro and *para*-bromo substituents reacted smoothly leading to cyclized products (**2g**, **2h**) in moderate yields. Similarly, *para*-methyl derivate **2i** was obtained in 71% yield. Electron donating substituent (methoxy), iodo- and electron with-drawing substituent (trifluoromethyl) on *para*-position were efficiently converted into the desired

Table 2. Scope of the Rh-catalyzed cyclization of succinimide derived 1,6-dienes **1**.[a,b,c]



Entry	[Ar^1]	[Ar^2]	2	Yield%
1	Ph	Ph	**2a**	87
2	3-BrC_6H_4	Ph	**2b**	60
3	3-ClC_6H_4	Ph	**2c**	62
4	3-MeOC_6H_4	Ph	**2d**	61
5	2-BrC_6H_4	Ph	**2e**	73
6	2-MeOC_6H_4	Ph	**2f**	87
7	4-ClC_6H_4	Ph	**2g**	66
8	4-BrC_6H_4	Ph	**2h**	60
9	4-MeC_6H_4	Ph	**2i**	71
10	4-MeOC_6H_4	Ph	**2j**	93
11	4-IC_6H_4	Ph	**2k**	80
12	4-$CF_3C_6H_4$	Ph	**2l**	85
13	2-naphthyl	Ph	**2m**	76
14	2-thiophenyl	Ph	**2n**	92
15	Ph	4-EtOC_6H_4	**2o**	82
16	Ph	4-$NO_2C_6H_4$	**2p**	57
17	Ph	4-*t*-BuC_6H_4	**2q**	86
18	Ph	3,5-diMeC_6H_3	**2r**	90
19	Ph	3,5-bis$CF_3C_6H_3$	**2s**	79

[a] Unless otherwise noted, the reaction conditions were as follows: **1** (0.2 mmol), silane (0.2 mmol), and in toluene (2.0 mL). [b] Isolated yield. [c] Dr value of **2** Determined by ^{1}H NMR (unless otherwise noted, the dr of **2** is generally $>20:1$).

products in high isolated yields (**2j** with 93%, **2k** with 80%, and **2l** with 85% respectively). Next, substitute bearing a 2-naphythenyl group reacted smoothly, providing the expected compound **2m** in 76% yield. Thienyl-substituted 1,6-diene was tested as well, the desired product **2n** was obtained in 92% yield.

To further extend the scope of application of our methodology, we next examined several *N*-aryl-succinimide based 1,6 dienes on the rhodium catalyzed cycloisomerization process. *Para*-position on the aromatic ring bearing an electron donating group, such as ethoxy and *tert*-butyl substituents reacted smoothly, giving the desired products (**2o** and **2p**) in good yields, whereas electron with-drawing group, *para*-nitro substituent gave the excepted compound **2q** in moderate yield. Finally, 3,5-dimethy and 3.5-bis(trifluoromethyl) substituents allowed the formation of the corresponding product (**2r** and **2s**) in 90% and 79% isolated yield, respectively.

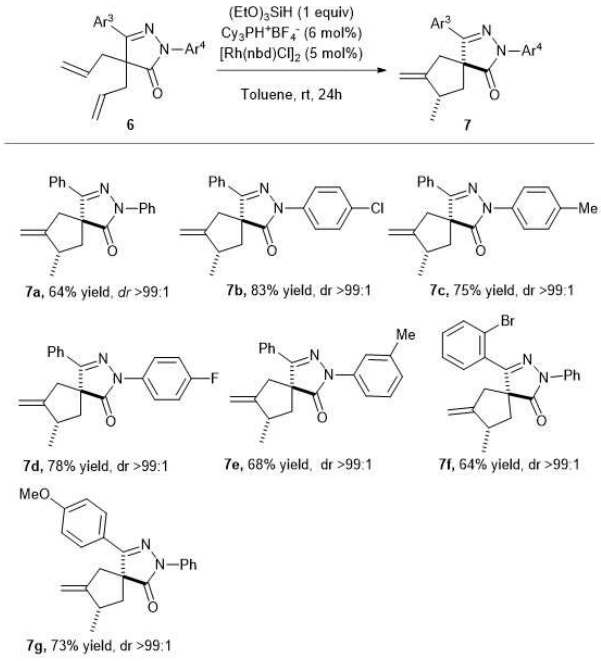
It is worth to mention that all the spiro-products were observed with a complete diastereoselectivity. The X-Ray crystallographic analysis of **2e** led us to unambiguously determine the relative and absolute configuration of the molecule (Table 2). Moreover, a gram scale reaction of **1a** provided the desired product **2a** without the erosion of isolated yield and diastereoselectivity.

In this stage, a kinetic study for the formation of **2a** was also performed and determined by GC analysis (see the ESI). According to the curve, **1a** could be converted into **2a** within 14 hours.

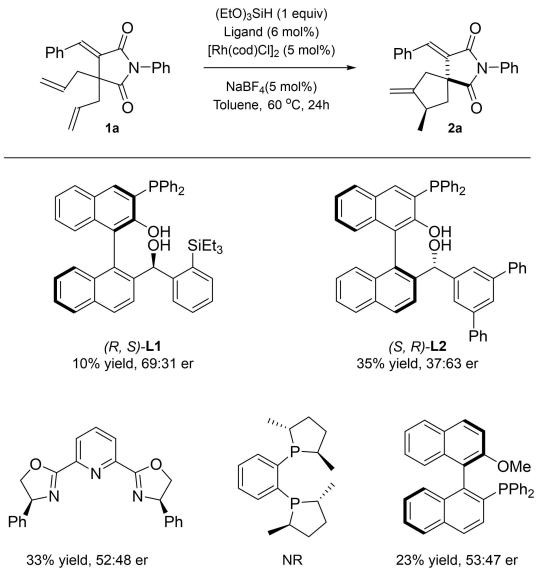
In addition, pyrazolones and related heterocycles are both common structural motifs in pharmaceutical agents, natural products and synthetic building blocks.[16] we consider using pyrazolone derived 1, 6-dienes as a backbone in the reaction to provide corresponding pyrazolone based spiro-derivatives, to demonstrate the versatility of the methodology that we developed: A highly diastereoselective rhodium catalyzed cycloisomerization of 1,6-dienes assisted by triethoxysilane.

Under the standard conditions as optimized above, several pyrazolone based 1,6-dienes, which modified with halogen atoms, methyl and methoxy on the aromatic ring were tested on the reaction system. To our delight, the cycloisomerization of pyrazolone based 1,6-dienes were proved suitable materials in this catalytic system, and to be a highly diastereoselective process. As shown in Scheme 3, substrates **6a**–**g** were reacted smoothly, afforded the excepted pyrazolone based spiro-products **7a**–**g** in 64–83% isolated yield as a single diastereoisomer.

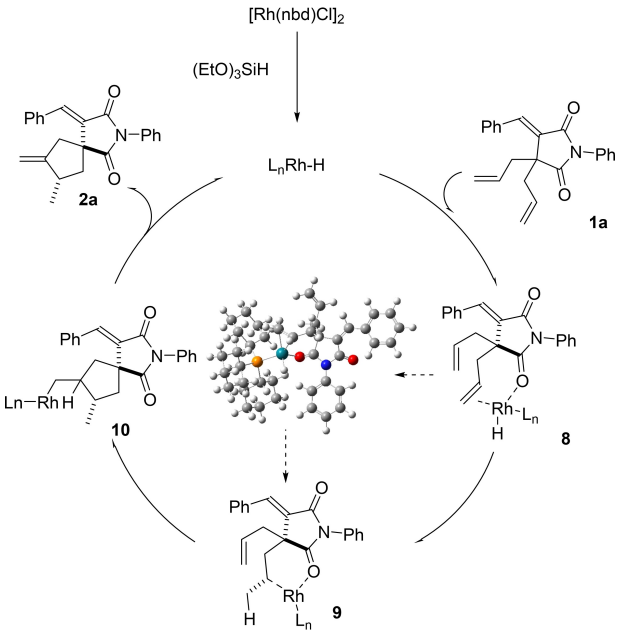
Then the attention was turned to the asymmetric synthesis of chiral spiro-fused heterocycles. Under the modified reaction conditions, several commercially available chiral phosphine ligands were examined. On the basis of a large amount of exploring experiments based on the screening of chiral P-ligands and reaction parameters, most of chiral P-ligands turned



Scheme 2. Rh-catalyzed cyclization of pyrazolone derived 1,6-dienes **6**. [a] Unless otherwise noted, the reaction conditions were as follows: **6** (0.2 mmol), silane (0.2 mmol), in toluene (2.0 mL). [b] Isolated yield.



Scheme 3. Enantioselective Rh-catalyzed cyclization of **1**. [a] Unless otherwise noted, the reaction conditions were as follows: **1 a** (0.2 mmol), silane (0.2 mmol), in toluene (2.0 mL). [b] Isolated yield. [c] ee determined by HPLC on a chiral stationary phase.



Scheme 4. Plausible mechanism for the hydrosilane-assisted Rh-catalyzed cycloisomerization.

out to be unsuitable partners in the construction of **2 a**, and no data of enantioselectivity was observed in this reaction. Such asymmetric rhodium-catalyzed cycloisomerization of succinimide or pyrazolone-derived 1,6-dienes is proved to be a highly challenging reaction because of no previous reports on the development of chiral P-ligand for this type of cycloisomerization reaction. Inspired by our previous investigations on the copper-catalyzed Huisgen cycloaddition reaction of succinimide-derived or pyrazolone-derived bisalkynes with azides in the presence of chiral phosphine ligand Tao-Phos,[17] we hypothesis that Tao-Phos and its analogues may show an ideal control of enantioselectivity on this rhodium-catalyzed cycloisomerization process.[17d] Unexpectedly, the asymmetric cycloisomerization of **1 a** was obviously suppressed in the presence of Tao-Phos. The expected product **2 a** was isolated as a single diastereoisomer albeit with low yields and promising enantioselectivities (Scheme 3). Among Tao-Phos and its analogues, (*R,S*)-**L1** provided the best enantioselectivity (69 : 31 *er*) and 37 : 63 *er* was observed in the presence of (*S,R*)-**L2** (see Scheme 3). It should be noted that, this result was still the best record in this reaction on the basis of our screening experiment of chiral P-ligands (*see* the Scheme S2 and Table S11 of Supporting Information).

Although the mechanism of rhodium-catalyzed cycloisomerization of 1,6-dienes remains unclear, we suggest that this hydrosilane assisted Rh-catalyzed cyclization process initiated to form a Rh–H species, supported by the observation of a new signal on ^{35}P NMR data (see the ESI) and literature precedence. As shown in Scheme 4, a plausible mechanism was proposed. First, the Rh–H species would accommodate one of the two C=C units with oxygen atom of imide moiety on **1 a** to form a hydride-diene complex **8**. In the next stage of oxidative addition, the Rh–H species could insert into one alkene moiety of **1 a**, followed by a re-insertion to another C=C bond of the intermediate **9** gives birth to the ring-formed intermediate **10**. Finally, the desired product was generated through β-H elimination. Notably, we believed that oxygen of imide moiety could coordinate with Rh center as a directing group, which would be beneficial to the excellent diastereoselectivity in the rhodium-catalyzed 1,6-cycloisomerization.

In summary, we developed an efficient catalytic diastereoselective synthesis of spiro-fused succinimide and pyrazolone derivatives. This methodology, using $(EtO)_3SiH$ assisted rhodium catalyst as the catalytic system allowed the formation of the spiro-fused succinimide and pyrazolone derivatives in moderate to high yields (57–93% yield) and excellent diastereoselectivity (>20 : 1). The broad range scope of the reaction offers a new protocol to synthesize spiro-fused succinimide and pyrazolone derivatives. The extension to asymmetric transformation of succinimide based 1,6-diene was also explored in the presence of Tao-Phos, which developed by our research group. Although the chiral control in this 1,6-diene cycloisomerization transformation is not perfect, but Tao-Phos is the only effective chiral phosphine ligand that can provide promising enantioselectivity so far. We believe this work will possibly inspire researchers to explore more effective ligands in this filed. Further effort to the development of an asymmetric version for the transition-metal-catalyzed cycloisomerization of 1,6-dienes are underway in our laboratory.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: rhodium · hydrosilane · diastereoselectivity · cycloisomerization reaction · 1,6-dienes

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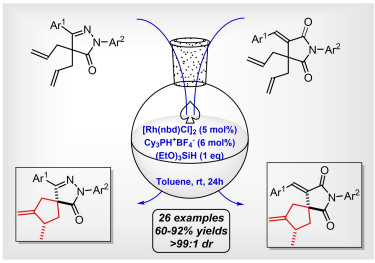
A highly diastereoselective rhodium-catalyzed cycloisomerization of 1,6-dienes that is promoted by hydrosilane has been established to afford spiro-fused succinimide and pyrazolone derivatives in moderate to excellent yields as a single diastereoisomer.



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Highly Diastereoselective Hydrosilane-Assisted Rhodium-Catalyzed Spiro-Type Cycloisomerization of Succinimide and Pyrazolone-Based Functional 1,6-Dienes